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PA-PTCDI for use in µc-Si:H solar cells: basic chemical and morphological effects

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Abstract

Basic research on N,N'-diallyl-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid diimide (Phenoxy-Allyl-PTCDI, short PA-PTCDI) is presented. Synchrotron photoemission spectroscopy is used in order to investigate a possible chemical interaction of PA-PTCDI on two differently treated silicon substrates. Additional AFM measurements investigate the influence that storage under ambient conditions has on the morphology of thin dye films.

Keywords: PA-PTCDI; Phenoxy-Allyl-PTCDI; Silicon; Si(111):H; SXPS; AFM

1. Introduction

Sensitizing inorganic indirect bandgap semiconductors with direct bandgap organic dyes is an attempt to improve present thin film solar cells. The idea is to increase the absorptivity and thus reach higher efficiencies and / or to decrease film thickness and thus production cost [1]. The approach followed by our group is to use small organic molecules embedded in hydrogenated microcrystalline silicon (µc-Si:H) and has been described earlier [1-3].

In the present paper several aspects of introducing an organic dye into a µc-Si:H matrix are discussed. The dye investigated here is a perylene diimide derivative, namely N,N'-diallyl-1,6,7,12-

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tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid diimide (Phenoxy-Allyl-PTCDI, short PA-PTCDI). Its structural formula can be seen in Fig. 1. In a preceding publication we already showed that PA-PTCDI layers can be produced in UHV at a sublimation temperature of around 280 °C and that the electronic lineup of PA-PTCDI with respect to silicon should in principle allow for a transfer of photo-generated charge carriers as the energetic positions of the PA-PTCDI HOMO and LUMO are below the valence band maximum and above the conduction band minimum of silicon, respectively [3].

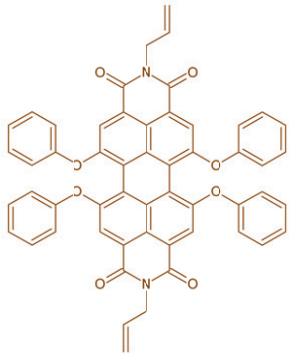

Fig. 1. Structural formula of $C_{54}H_{34}N_2O_8$, short PA-PTCDI

Here we investigate a possible reaction of PA-PTCDI with hydrogen terminated silicon by synchrotron induced X-ray photoemission spectroscopy (SXPS) in order to deduce if the molecule properties will be preserved in a µc-Si:H environment. In addition in AFM measurements the PA-PTCDI behavior under ambient conditions is studied.

2. Experimental

2.1. Interface investigation with focus on chemical reactivity between silicon and PA-PTCDI

Microcrystalline silicon usually contains a double-digit volume percentage of hydrogen which terminates dangling bonds of the silicon. Therefore we expect the dye to be surrounded by Si:H. Because µc-Si:H production depends on many process parameters and is thus subject to irregularities we use a hydrogen terminated silicon wafer as a model substrate for dye deposition. This material has been studied extensively [e.g. 4,5] and due to the good reproducibility allows for the attribution of the observed effects to the respective materials.

The experiments were performed in the integrated solid/liquid analysis system SoLiAS [6] located at the undulator beamline U49/2-PGM2 at BESSY II. The beamline provides photons in the energy range between hν = 80 – 1500 eV, permitting a wide range of surface sensitive core level SXPS. The photoemission spectra are recorded with a hemispherical analyzer Phoibos 150 (Specs) under an 18° emission angle of the photoelectrons relative to the sample normal. The base pressure in the analyzing chamber was at 3 x 10^{-10} mbar.

For the interface experiments described here we used n-doped silicon wafers (IXYS) grown in [111] direction with a 4 µm thick epitaxial overlayer and a phosphorous concentration of 2.5 x 10^{16} cm^{-3}. The wafers were covered with a native oxide of about 1.2 nm thickness as calculated from SXPS data. For the first experiment the native oxide on Si(111) was removed with a two-stage etching process in ammonium fluoride resulting in a hydrogen termination of the surface [3]. The dye is assumed to grow in an environment containing not only well-passivated Si:H but also dangling bonds on a rougher scale than the

usually atomically flat Si(111):H so that in a second experiment the oxide of a Si(111) wafer was sputtered away with Argon ions in order to provide a rougher and more reactive surface.

PA-PTCDI was sublimed from home-made evaporation cells of the Knudsen type with a deposition rate of 0.25 nm/min. The deposition chamber had a base pressure of 3 x 10^{-8} mbar. After the measurement of the respective silicon substrates PA-PTCDI was deposited stepwise onto the sample and measured with synchrotron radiation in the range of 90 – 600 eV using a pass energy of 10 eV in order to ensure high surface sensitivity as well as high energy resolution. The Si2p emission was measured with photon energies of 130, 150 and 155 eV with a pass energy of only 5 eV, resulting in an even better resolution and ensuring highest surface sensitivity. Binding energies were corrected with respect to the Fermi edge of a clean silver sample. The experimental resolution as determined with the FWHM of the silver sample Fermi edge was 230 meV for a pass energy of 10 eV and 160 meV for a pass energy of 5 eV. The film thickness was calculated from the damping of the Si2p emission line. This includes a calculated inelastic mean free path for electrons in PA-PTCDI of 0.55 nm according to the formula developed by Tanuma, Powell and Penn [7] for a kinetic energy of 50 eV and assuming a dye density of 1.5 g/cm^3.

2.2. Morphological investigation of PA-PTCDI

The perylene derivative Cl_4MePTCDI, whose structure is very similar to that of PA-PTCDI, is known to form crystalline structures when stored under ambient conditions [8]. The crystallites can reach sizes visible to the human eye which has of course important impacts on the intended use of the organic dye: the charge carrier mobility as well as the charge carrier lifetime increase with increasing crystallinity, the absorption and emission spectra change and the initially weak intermolecular interaction becomes larger [8]. Also larger dye clusters automatically imply less interface area if the same amount of material is used, which might hinder efficient charge transfer.

In order to investigate if PA-PTCDI exhibits the same changes, layers of PA-PTCDI were deposited onto quartz glas and investigated by AFM (MFP-3D, Asylum Research) in intermittent mode with n-doped silicon tips on air. One sample was measured directly following preparation, another one was measured after storage under ambient conditions for ten weeks. The pictures were then evaluated using WSxM [9].

3. Results

3.1. Interface investigation with focus on chemical reactivity between silicon and PA-PTCDI

The photoemission spectra of the dye deposited onto Si(111):H and onto sputtered Si(111) are shown in Figures 2 – 4. The survey spectra (cf. Fig. 2) show the pure silicon substrate and the subsequent evolution of the characteristic emission lines of PA-PTCDI with increasing film thickness on both samples. The substrates exhibit some residual contamination with oxygen and carbon. For the etched sample, this is attributed to hydrocarbons and suboxides which are adsorbed / formed in the short time between the end of the etching procedure and the insertion of the sample into the UHV load lock. For the sputtered sample, the emission lines probably stem from former surface contaminations that were buried in the silicon due to the sputter process. In addition Argon from the sputter process is visible for this sample.

The Si2p detail spectra recorded with a photon energy of 150 eV are shown in Fig. 3. The silicon detail spectra recorded with photon energies of 130 eV and 155 eV show slightly different secondary electron background intensities, but the major features remain the same, so that they are not shown here.

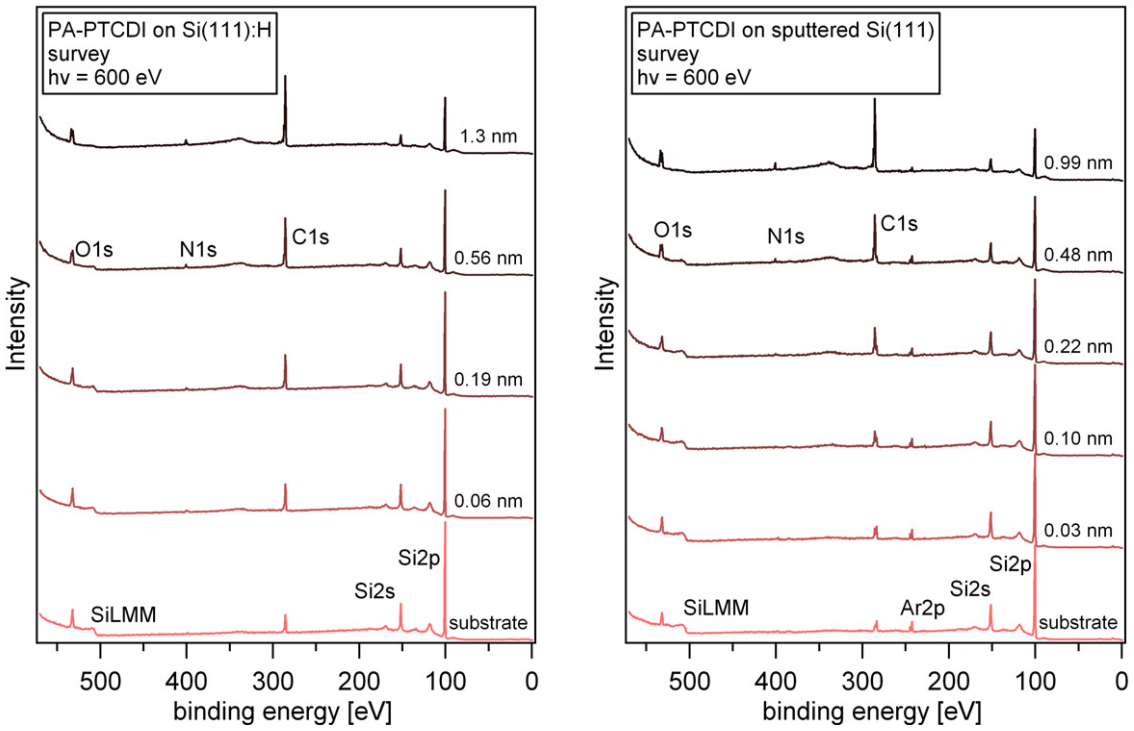

Fig. 2. SXPS Survey spectra showing the formation of a thin PA-PTCDI layer on silicon. Left: Si(111):H, right: sputtered Si(111).

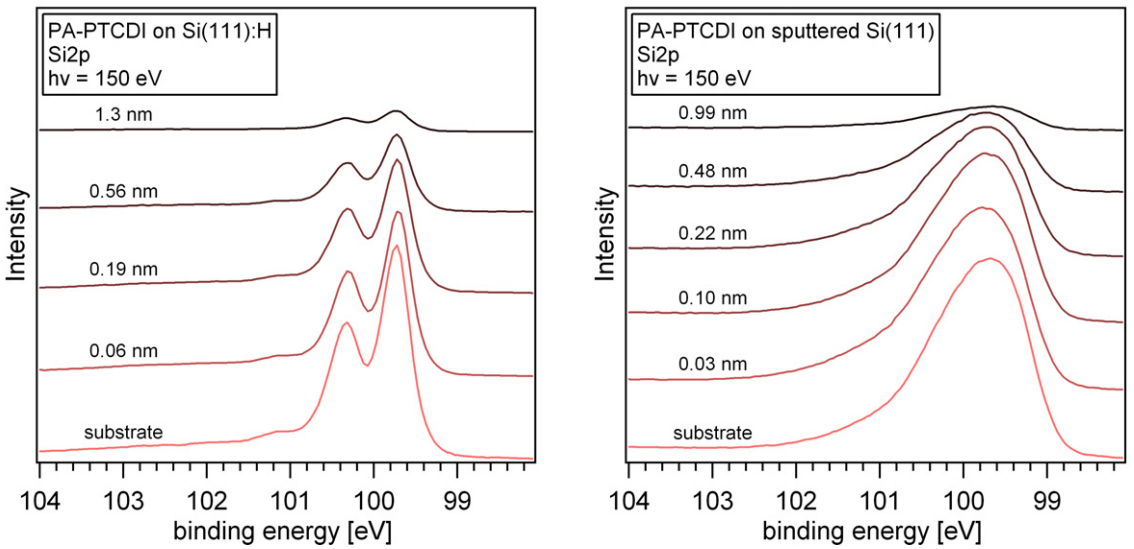

Fig. 3. SXPS Si2p detail spectra being damped with increasing PA-PTCDI layer thickness on silicon. Left: Si(111):H, right: sputtered Si(111).

No completely oxidized silicon component is visible in the Si2p spectra, just some minor suboxides at a binding energy of around 101 eV. With increasing PA-PTCDI film thickness the Si2p signal is damped. For the etched sample the spin orbit splitting is clearly resolved. For the sputtered sample it is evident that the sputtering had the desired effect of roughening the surface. This is deduced from the broadening of the Si2p emission for which the doublet cannot be resolved anymore due to a loss of long-range order.

For further analysis the Si2p spectra were normalized in intensity and shifted in energy to account for the small band bending that is induced by the interface formation [3]. These spectra are depicted in Fig. 4. For the etched sample no chemically shifted component appears at higher binding energies as would be expected if a reaction took place [10]. The same holds true for the sputtered substrate, even though here this is harder to detect due to the broadening of the emission line. Thus the dye seems to be chemically unaffected by the presence of the silicon and the optical properties should simply add up in a composite material.

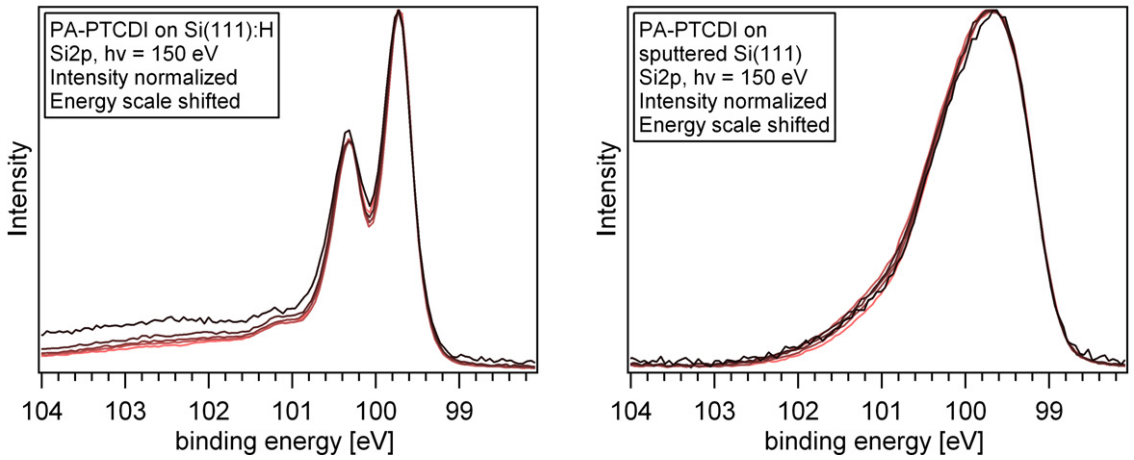

Fig. 4. SXPS Si2p spectra from Fig. 3, normalized with respect to intensity and shifted in energy to account for band bending at the interface to silicon. Left: Si(111):H, right: sputtered Si(111).

3.2. Morphological investigation of PA-PTCDI

The AFM pictures obtained from the freshly prepared and the stored sample are shown in Fig. 5. The full z scale corresponds to 7.6 nm on the left hand side and 68 nm on the right hand side, the r.m.s. values are 0.95 nm and 10.4 nm, respectively. As can be clearly seen on the left hand side, no defined structures are visible directly after preparation. The few white spots are ascribed to contaminations on the surface from the surrounding air, the straight lines can be attributed to scratches already present on the substrate. On the other hand the stored sample shows very nicely the formation of large crystalline clusters that are forming islands which even seem to retreat from the substrate that was covered before. These island structures are visible to the eye in their lateral dimensions and cover the whole sample.

As already mentioned in section 2.2, an increase in crystallinity should lead to a higher charge carrier mobility as well as charge carrier lifetime. These effects would be beneficial if they occurred in a solar cell because electrical losses could be potentially reduced. On the other hand a higher crystallinity will probably be accompanied by a smaller total interface area, which might hinder an efficient charge transfer from the dye to the silicon. Altogether it is not clear so far if the crystallization will reduce or even further enhance the performance of solar cells made with PA-PTCDI embedded in μc-Si:H compared to solar cells made from μc-Si:H only.

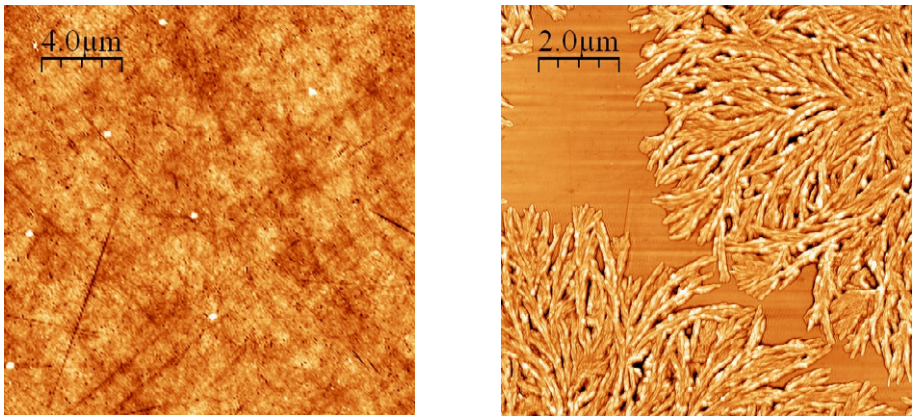

Fig. 5. AFM pictures of a freshly prepared PA-PTCDI layer (left) and a PA-PTCDI layer stored under ambient conditions for ten weeks (right)

4. Conclusions

The insertion of PA-PTCDI in µc-Si:H as a sensitizing organic molecule for use in solar cells was investigated on a basic research level. We observed no reaction of silicon and PA-PTCDI, indicating that the dye is chemically unaffected by the presence of the silicon. This result implies that the optical properties of both single materials should simply add up in a composite structure. The morphology after preparation of PA-PTCDI layers shows no distinct features, whereas after storage in air crystallites are formed. Up to now it is not clear if this effect will have a positive or negative influence on the intended employment of the dye because both possibilities can be supported by plausible arguments.

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References

[1] T. Mayer, U. Weiler, E. Mankel, W. Jaegermann, C. Kelting, D. Schlettwein et al., Renew. Energ. 33 (2008), 262 – 266

[2] T. Mayer, U. Weiler, C. Kelting, D. Schlettwein, S. Makarov, D. Wöhrle et al., Sol. Energ. Mater. 91 (2007), 1873 – 1886

[3] A. Decker, S.-L. Suraru, O. Rubio-Pons, E. Mankel, M. Bockstedte, M. Thoss et al., submitted

[4] G. S. Higashi, Y. J. Chabal, G. W. Trucks, and Krishnan Raghavachari, Appl. Phys. Lett. 56 (1990), 656 – 658

[5] G. S. Higashi, R. S. Becker, Y. J. Chabal, and A. J. Becker, Appl. Phys. Lett. 58 (1991), 1656 – 1658

[6] T. Mayer, M. Lebedev, R. Hunger, and W. Jaegermann, Appl. Surf. Sci. 252 (2005), 31 – 42

[7] C. Powell and A. Jablonski, NIST electron inelastic-mean-free-path database version 1.1, National Institute of Standards and Technology, Gaithersburg

[8] H. Graaf, T. Unold, C. Mattheus, and D. Schlettwein, J. Phys. D Appl. Phys. 41 (2008), 105112

[9] I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, and A. M. Baro, Rev. Sci. Instrum. 78 (2007), 013705

[10] J. Terry, M. R. Linford, C. Wigren, R. Cao, P. Pianetta, and C. E. D. Chidsey, J. Appl. Phys. 85 (1999), 213 – 222